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Formation of Biphasic State in Vacuum-Arc Coatings Obtained by Evaporation of Ti-Al-Zr-Nb-Y Alloy in the Atmosphere of Nitrogen

V.M. Beresnev[1,*], O.V. Sobol[2], I.N. Toryanik[1], A.A. Meylekhov[2], U.S. Nyemchenko[1], P.V. Turbin[1,3], I.V. Yakushchenko[1], M.O. Lisovenko[1]

[1] *Karazin Kharkiv National University, 4, Svobody Sq., Kharkiv, Ukraine*
[2] *National Technical University «Kharkiv Polytechnic Institute», 21, Frunze Str., Kharkiv, Ukraine*
[3] *Scientific Center of Physical Technologies of Ministry of Education and Science and National Academy of Science of Ukraine, 6, Svobody Sq., Kharkiv, Ukraine*
[4] *Sumy State University, 2, Rymskogo-Korsakova Str., Sumy, Ukraine*

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By means of X-ray diffraction, transmission and scanning electron microscopy, energy dispersive spectroscopy and indentation methods, the effect of nitrogen atmosphere pressure on composition, structure and hardness of vacuum-arc (Ti-Al-Zr-Nb-Y)N coatings during the deposition process has been studied. The two-phase state of the coating with solid-solution metal component (bcc lattice) and nitride phase (fcc lattice) have been formed. Increasing the pressure of nitrogen atmosphere leads to the increase of nitrogen component in the coating as well as to increase of the ordering regions size, allowing to achieve the hardness of $H = 49$ GPa at a pressure of $P = 0.5$ Pa.

Keywords: Vacuum-Arc Deposition Method, Mechanical Characteristics of Coatings, Refractory Metal Nitride Coatings.

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1. INTRODUCTION

The two-phase state of the coatings material is characterized by two components: the solid one and the relatively soft one. This helps to improve the mechanical properties and strain relaxation in the contact region during the functional use of protective coatings [1, 2]. One of the possible applications of such coatings is the surface layer of the cutting tools [3–7]. During the formation of the coatings based on nitrides, the two-phase state is achieved by using multi-element alloy cathodes. The constituent elements of the alloys are characterized by different enthalpy of formation of nitride phases [8, 9].

The aim of the study is to analyze the effect of nitrogen pressure on the following factors: composition, structure and mechanical properties of vacuum-arc coatings obtained by evaporation of Ti+Al+Zr+Nb+Y alloy, which combines nitride forming elements such as (Ti, Al, Zr), and elements having a relatively small value of absolute formation enthalpy (Nb and Y).

2. METHODS OF COATINGS' OBTAINIG AND ANALYZING

The samples with the coatings (Ti-Al-Zr-Nb-Y)N were obtained in the experimental vacuum-arc setup "Bulat-6". To improve the strength characteristics of the coating and its adhesion characteristics, the constant negative bias potential of $U_b = -150$ V was applied to the substrate of stainless steel 12X18H9T. The current of the arc discharge in the evaporator was varied from 100 A to 110 A. The nitrogen pressure was varied in the range: $P = 0.05$-0.5 Pa during the deposition. The thickness of the obtained coatings was $d = 8.0$-9.0 μm.

Study of structurally stressed state was carried out on DRON-3M diffractometer in the Cu-Kα radiation. The graphite monochromator was used to monochromatise the detected radiation. It was set in the secondary beam (before the detector). Studies of the phase composition, structure, substructure and texture were carried out by conventional methods of X-ray diffraction techniques, i.e., by analyzing the position, intensity and shape of the diffraction reflexes profiles. To decrypt the diffraction patterns, the tables of The International Centre for Diffraction Data "Powder Diffraction File" were used. Substructural characteristics were determined by the approximation method [10].

The structure of the coatings was investigated by analytical methods of electron microscopy: transmission microscope (JEOL-2100) and scanning microscope (FEI Nova NanoSEM 450). Chemical analysis of the elements was carried out by means of energy dispersion X-ray spectroscopy using EDAX spectrometers, which is the part of scanning electron microscope equipment.

The hardness of the obtained coatings based on (Ti-Al-Zr-Nb-Y)N was determined with a help of DM-8 device at a load of 200 g.

3. RESULTS AND DISCUSSION

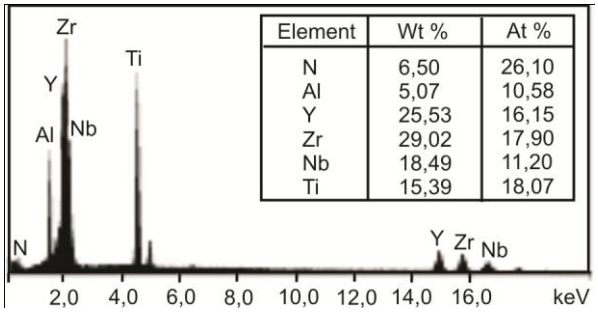
The elemental composition spectra, obtained by energy dispersion analysis, are shown in Fig. 1.

The structural state study, carried out by the X-ray diffraction method, has shown that coatings obtained at the lowest pressure (0.05 Pa) have a phase with bcc lattice as a crystalline phase, which is typical structure of high entropy alloy without formation of own nitride lattice [11]. Apparently nitrogen present in the coating in this case creates formations with amorphous struc-

* beresnev-scpt@yandex.ru

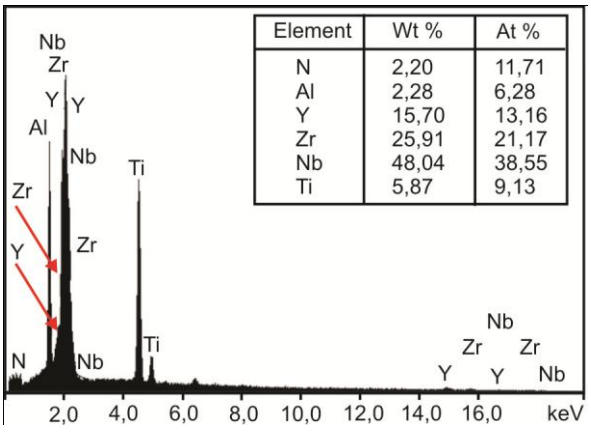
ture, which can be observed as a "halo" in the range of angles $2\theta \approx 31$-42 degrees with a maximum at an angle $2\theta \approx 36$ degrees.

Analysis of the spectra showed that concentration of the nitrogen component in the coatings varied from 7.11 at.% (at $P = 0.05$ Pa) and 1.26 at. % (at $P = 0.3$ Pa) to 35.42 at.% at $P = 0{,}5$ Pa in the used range of pressures. The content of metal components for Al : Ti : Zr : Nb : Y was observed in proportion of 5 : 9 : 10 : 5 : 6 respectively.



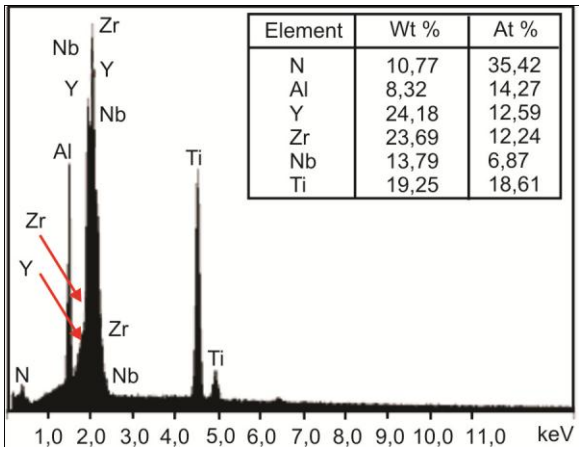
Element	Wt %	At %
N	6,50	26,10
Al	5,07	10,58
Y	25,53	16,15
Zr	29,02	17,90
Nb	18,49	11,20
Ti	15,39	18,07

a



Element	Wt %	At %
N	2,20	11,71
Al	2,28	6,28
Y	15,70	13,16
Zr	25,91	21,17
Nb	48,04	38,55
Ti	5,87	9,13

b



Element	Wt %	At %
N	10,77	35,42
Al	8,32	14,27
Y	24,18	12,59
Zr	23,69	12,24
Nb	13,79	6,87
Ti	19,25	18,61

c

Fig. 1 – Energy dispersion spectra of the coatings, obtained at different nitrogen pressures: a – $P = 0.05$ Pa, b – $P = 0.3$ Pa, c – $P = 0.5$ Pa

The size of the bcc phase crystallites is small enough, it is equal 7.7 nm. Estimating of the phases content in the coating by the ratio of the integral intensities shows, that it is close to 2/1 – for the bcc phase and for phase in amorphous-like condition respectively.

For coatings obtained at a higher pressure of working atmosphere of 0.3 Pa (Curve 2 in Fig. 2) the crystalline state becomes apparent for a component phase with a bcc crystalline lattice as well as for the nitride (Ti-Al-Zr-Nb-Y)N phase with fcc lattice (structural type NaCl). The size of the crystallites of the bcc phase was about 11.5 nm, and for the nitride fcc phase it was about 5 nm. Lattice period, determined by the position of diffraction peak maximum, was 0.462 nm. The ratio of bcc and fcc phases is close to 1/2.

Analysis of the third spectrum which characterized the coatings obtained at the highest pressure of $P = 0.5$ Pa shows, that coating has a higher degree of crystallinity of the constituent phases with the determining content of the fcc phase (the content of bcc and fcc components has a ratio of 1/3). The size of bcc phase crystallites is about 10 nm, and the size of nitride fcc phase crystallites is close to 7 nm. Defined by the position of maximum, the lattice period is 0.453 nm.

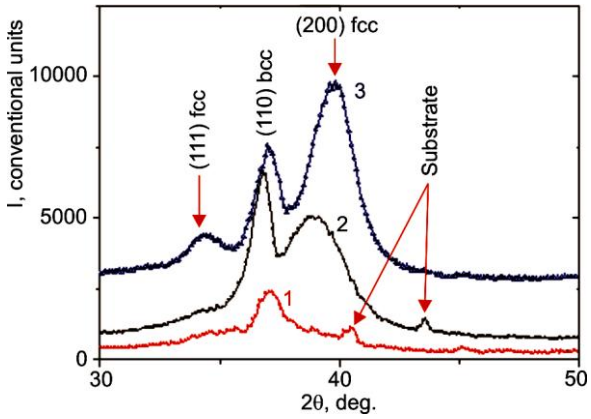


Fig. 2 – Areas of diffraction spectra of the coatings deposited at different pressures of nitrogen: curve 1 – $P = 0.05$ Pa, 2 – $P = 0.3$ Pa, 3 – $P = 0.5$ Pa

Analysis of the obtained results shows that the appearance of bcc phase in the coating is caused mainly by the droplet phase, which has a crystal structure at all the used pressures of nitrogen during the deposition process.

Fcc crystal lattice corresponds to the nitride phase. With the increase of pressure, the size of the ordering regions increases. It varies from amorphous-like state at the lowest pressure with the content of nitrogen atoms in the coating of about 12 at.% to nanocluster state with the size of ranked structural formations of 5 nm at an average pressure, when the content of nitrogen atoms in the coating is 26 at.%. And then nanocrystalline state appears at the maximum pressure with the content of nitrogen atoms in the coating of 36 at.%.

Fig. 3 shows the microstructure image of the coating based on (Ti-Al-Zr-Nb-Y)N and microdiffraction from the selected area (see Fig. 3a). Microdiffraction obtained from this area corresponds to the fcc lattice with a period close to the one obtained by X-ray analysis.

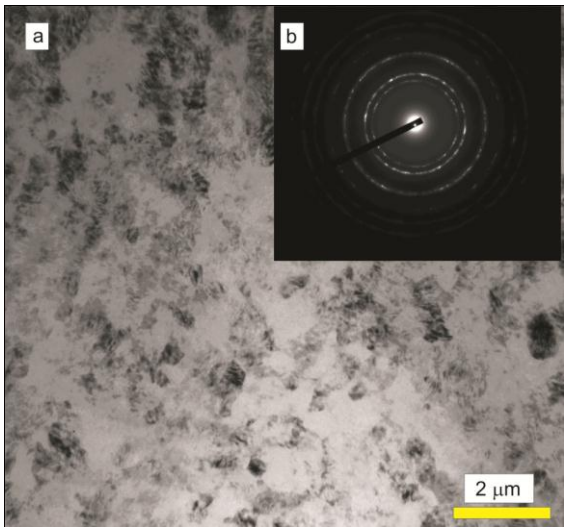


Fig. 3 – Image of microstructure of the coating based on (Ti-Al-Zr-Nb-Y)N obtained at nitrogen pressure $P = 0.3$ Pa (a) and microdiffraction pattern of the selected area (b)

Measurement of such a universal mechanical characteristic of the coating as hardness showed, that with the increase of nitrogen pressure the hardness of samples varies from 34 GPa at the lowest pressure to 49 GPa at the highest pressure and the content of nitrogen of 36 at.%.

4. SUMMARY

Thus, the structure of the coating formed at low pressure of the nitrogen atmosphere is the least thermodynamically stable, which determines the lowest hardness of the coatings. Increasing the pressure brings the system to a more stable state with a biphasic structure, resulting in increased hardness of up to 49 GPa.

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